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**THE DISTRIBUTION OF CARBON AND
HYDROGEN IN THE PRODUCTS OF
LOW TEMPERATURE COKING**

BY

HARVEY WOOLSEY HYDE

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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ENTITLED.....THE DETERMINATION OF CARBON AND HYDROGEN IN COAL,.....

.....COKE AND TAR AND THEIR DISTRIBUTION IN THE PRODUCTS OF THE.....

COKING OF THE COAL

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF.....BECHELLOR OF SCIENCE.....

.....
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THE DETERMINATION OF CARBON AND HYDROGEN
IN COAL, COKE AND TAR AND THEIR DISTRIBUTION IN
THE PRODUCTS OF THE COKING OF THE COAL

I. INTRODUCTION

For the past few years great interest has been manifested in any experiments made with a view of commercializing a process for the low temperature coking of coal. The University of Illinois, through Professor S. W. Parr, can be rightly considered the leader in this work.

During the past year Professor S. W. Parr and Doctor T. E. Layng have been conducting a series of coking experiments with a view to publishing more exact data on what can rightly be expected as the average yields of products resulting from low temperature carbonization. This work has been made necessary on account of the many reports brought to their notice of extravagant yields.

The coking experiments were made in an electrically heated retort especially built for this purpose by Dr. T. E. Layng. The Parr-Layng coking process was used in all their tests.

The tests on the different types of coal were stabilized as much as possible in order to obtain comparable data. It was hoped that under similar conditions, the yields of the various products would be constant and that very little difference in their chemical composition would result. It was also hoped that evidence might be found in the distribution of the carbon and hydrogen in the products, which would clear up some of the unknown factors encountered in coking different types of coal.

The method pursued was one of analysis for the two components, by means of combustion of the material in an atmosphere of oxygen,

and the collection of the products formed. The procedure was the same as for any combustion determination. The early part of the work was done with a Glasier type, gas fired furnace, but it was supplanted by an electric furnace, owing to its difficulty of control.

The report on the ultimate analysis for carbon and hydrogen given in the papers of the American Society of Testing Materials was followed as to the setting up of furnace and absorption trains. Later, modifications were made to meet conditions. Wagner¹ also discusses this method of determination. The method outlined below seems, however, to be better adapted for the work on this problem. No references to the combustion of tars for the determination of carbon and hydrogen were found and the technic was developed as the work progressed.

II. EXPERIMENTAL

The Furnace-

A gas fired combustion furnace of the Glasier type was used during the first part of the work. It was found to be unsatisfactory. The variations in the heat of the gas made it very difficult to control and keep it at a constant temperature.

An electric furnace of the organic combustion type replaced the gas furnace in the latter part of the work, and, because of its ease of control, gave excellent results. This furnace consisted of three heating units, connected in parallel, with a

1. Wagner--Coal and Coke, p. 75

controlling rheostat for each unit, allowing a very close regulation. The units were well insulated and so arranged as to be replaceable when damaged. Two coils in series composed a unit and they were set in hinged sections, which allowed easy examination of the parts of the furnace. The tubes rested on a brass channel piece inside the furnace, so that it was entirely surrounded by heating coils when the sections were closed.

Reagents-

Granulated fused calcium chloride in glass stoppered Marchand tubes saturated with CO_2 were used to absorb the moisture produced in the determination.

A saturated solution of C. P. caustic potash in a Bender and Hobbein bulb was the medium of absorption for the carbon dioxide. A guard tube containing soda lime and calcium chloride was attached to, and weighed with this bulb, to prevent the escape of any moisture or carbon dioxide. These tubes were closed by means of rubber policemen immediately after the run was finished and were kept closed during weighing.

As a further guard a Marchand tube containing soda lime and calcium chloride was placed at the end of the train to prevent moisture or carbon dioxide from drawing back into the weighing tubes.

The oxygen for the combustion was furnished from a cylinder of the compressed gas and controlled by a needle valve. It was passed through a Taubert Drying apparatus to remove any ammonia, carbon dioxide or moisture before entering the combustion tube.

The gas was admitted at a rate of two to three bubbles per second in this apparatus. Faster admission tended to prevent complete absorption of the carbon dioxide in the caustic potash. Aspiration was attempted, but the same tendency was noted and it was not successful. By the use of tight fitting rubber connections and short distances between pieces of apparatus, the pressure maintained in the system was not sufficient to cause leaks. Careful tests were made to determine the tightness of the set up before each run.

The Combustion Tube-

The combustion tube was of hard glass, one meter long. At first Jena tubes were tried, but they gave poor service. Japanese hard glass was but little better. Pyrex tubes gave the best results, and were used entirely after the first few weeks. The center 60 centimeters were filled with copper oxide, held in place by copper gauze rolls. One end was filled to about 5 centimeters of the end with fused lead chromate, also held by a copper gauze roll. The copper oxide forms the oxidizing region when heated and the lead chromate acts as an absorbing agent for the sulphur compounds formed during the combustion. These tubes were carefully burned out in an atmosphere of O_2 before any runs were made.

Considerable difficulty was experienced with these tubes at first, but the trouble was overcome. According to Terres,² methane does not burn to carbon dioxide and water in the presence of copper oxide below a red heat. The temperature of combustion

2. J. Gasbel 56, 8-11 (1915)

in O_2 is much lower, but it was found necessary to keep the furnace at about $700^\circ C.$ in order to insure complete combustion. To maintain this heat with the gas furnace it required constant watching and a temperature most of the time above $700^\circ C.$ to take care of the great variations due to pressure and heat value of the gas. This high temperature caused softening and swelling of the tube, uneven heating, fusion of the glass with the copper oxide or lead chromate and limited the life of the tube to a few runs. The greatest trouble was experienced with the section containing the lead chromate. The glass and reagent fused forming a low melting, brittle silicate, incapable of withstanding the gas pressure, and resulting in a bubble blowing out at that point. This brittle region was broken by the slightest movement.

The electrically heated furnace was very readily controlled to a heat of $700^\circ C. \pm 10^\circ C.$ by the use of rheostats and a thermocouple, and, the heat being even, a much longer life of the combustion tube resulted.

The difficulty in the gas furnace was overcome by wrapping the section of the tube containing the reagents with sheet asbestos and then placing the tube in a two-foot section of inch and a quarter iron pipe. The usual tube supports were removed from the center of this pipe and the gas flames allowed to play on it directly. The pipe did not enclose the section containing the boat, of course, which rested on a bed of silex. Such an arrangement made a rigid tube and pipe. It prevented swelling beyond the size of the pipe and prolonged the life of the tube by

about three times its usual period. When the tube broke, the parts were removed by shattering with cold water and shaking them out.

The same asbestos wrapping was found to aid materially in the electric furnace. Over 150 determinations were made on two such tubes in the electric furnace.

The method of application of the covering is simple. Fill the tube as desired. Cut a strip of thin asbestos about 26" long and 6" wide. Soak with water and roll the tube up in it. By rolling tightly and pressing the edge closely the wrapping will adhere to the tube when dry.

Method For Coal

Good results in this work depend largely on temperature control, 700° C. being the minimum for these materials because methane is one of the products of the distillation.

Two-tenths of a gram of coal, air dried, were placed in a small porcelain boat and kept in a closed tube till ready to be used. The furnace was previously heated to 700° C. in the last two coils and about 300° in the first coil. While oxygen was being run through the tube the absorption bulbs were placed and connected and the whole tested for leaks.

The coal sample was quickly slipped into the combustion chamber and followed by a hot copper roll to prevent moistures condensing at that end of the tube. The gas connections were made at once and the forward heater set to reach 700° C. After

the boat was burned clean and the tubbles showed no sign of further absorption, the run was continued 10 minutes, the bulbs removed and the gain in weight obtained. Hot tiles from a gas furnace had to be placed over the collection end of the combustion tube to prevent condensation of moisture there.

Coke

This is the same as for coal except that the forward heater can be at a higher temperature at the start with safety. The temperature of the whole apparatus can be lower because there is no methane in coke.

Tar

The samples of tar were weighed from a tube with a glass tube dropper for taking the sample. About five-tenths of a gram was taken for a run. The first coil section must be cold or too great evolution and evaporation of volatile products will spoil the determination. As soon as the sample is enclosed in the tube the heater is turned on to reach 700° C.

There are three stages in the combustion of tar. 1st. Expulsion of volatile products and rapid passage of gas through absorption bulbs. 2nd. Burning of high boiling products, and moderate gas passage into bulbs. 3rd. Burning of pitch.

There is a distinct pause between each step, but a greater one between the 2nd and the 3rd than between the 1st and the 2nd.

III. DISCUSSION

The coals used in these test runs are listed in Table III

with their corresponding numbers in the other tables. The object of the experiments was to determine the action of these types of coal in a low temperature coking process. A Pocahontas coal, representing the coking type, a Pittsburgh gas coal, a Jellico coal and four different types of Illinois coking coals composed the samples. By means of low temperature coking it is thought that all caking coals may be made to coke. It was also thought to show that all the products would be the same. To obtain more comparable percentages, the data was calculated to the moisture free basis.

The percentage data was averaged in the case of each type of coal, and plotted graphically to show the relation between the elements present in each sample. In Table IV the ordinates represent the percentage of carbon and the abscissas the percentage of hydrogen. The carbon percentages of Illinois coals are about 60% and for Pocahontas they are a little above 80%, while the hydrogen is about 5% in all coals. All graphical points will fall in the range of 50-90% carbon and 4-6% hydrogen, and these were set as the limits on the graphs.

In examining the data, it was found that the hydrogen in the coal, exclusive of that in the form of moisture, is very nearly a constant percentage. For all types of coals, the percentages varies between 4.18 and 5.58%, the average being about 5%. The data for the same kind of coal varies as much as does that for a very different type.

Oxidation in coal is recognized factor, but since check re-

sults were obtained in all cases, it indicates that it is a relatively slow process and is not a factor in analysis made by the combustion method. The difference in the hydrogen content is explained by the fact that there is some difference in the samples of the same coal. Sampling conditions also may be a factor which would cause variations in the analysis. These results are taken as showing that the hydrogen in coal is approximately constant for all coals of the caking type.

The carbon, on the other hand, is a great variable. Different types of coals show widely different percentages of carbon. The Illinois coals show carbon from 39.25% in Vermillion County to 74.50% in Saline County. The Eastern gas coals of the Pittsburgh gas type and the Jellico samples show a higher average content than these.

Carbon and hydrogen are believed to be present in coal in the form of hydrocarbons. Since there is a constant percentage of hydrogen and a varying percentage of carbon present in these different types, it must indicate that the hydrocarbons in the different kinds of coal are not the same.

From the general consideration of the coal data and the knowledge that Pocahontas and Pittsburgh coals are considered the best coking and gas coals and that Illinois coals, as Vermillion County coal, are not coking coals, it might be said that coals high in carbon give the best coke. This is the case in high temperature practice, but these tests show that such is not exactly true. Pocahontas runs highest in carbon in these

samples and vermillion County coal runs lowest, but very good coke was made from each by this process.

Coke

The data obtained from the analysis of coke were treated in the same manner as that of the coal, i.e., the results were reduced to the moisture free basis and averaged for the same types of coal. The resulting percentages were plotted graphically in Table V.

The hydrogen in coke is also a constant. The limits are 1.09 and 1.95%, with as large a variation in results from the same coke as from different kinds of coal. The average is about 1.50%. Metallurgical is very low in hydrogen and is very hard and firm. Coke from this process is hard and firm, but runs comparatively high in hydrogen. It may be looked on as an advantage since it aids in the combustion of the product. All the samples of coke showed excellent physical condition and compare favorably with metallurgical coke.

Since there is a definite percentage of hydrogen from the coal left in the coke it would indicate that certain hydrocarbon compounds in coal cannot be broken down or else new compounds are formed which are not decomposed at the final temperature of coking.

Tars

The percentage data for the tars were treated as in the case of coal and coke.

The composition of the tars from these test runs show great

similarity as regards their content of carbon and hydrogen. All types of coal give approximately the same percentages of these components and, as in the case of the coke, there is as great a variation in the composition of tars from the same type of coal as there is in tars from different kinds of coal. The percentage of carbon is more constant than it is in coke and the variation in percentage of hydrogen is much greater.

Since in the most carefully controlled process light differences will occur in the factors concerned, a difference is to be expected in the products of such a process. In this case there were differences of temperature, pressure and other working conditions which would effect the products even though the differences were very small. From this, since the tars are so similar in composition and character, it may be taken that the heat is the controlling factor in their formation and that under exactly similar conditions the percentage of carbon and hydrogen in the tars would be constants. It is evident that it is impossible to make tars of exactly the same character by this process.

While the carbon and hydrogen content of tars from different types of coal do not vary greatly, the yields of tar depend definitely on the type of coal. This indicates that whereas the amount of condensible volatile products varies with the types of coal, on carbonization the condensible volatile products produced are much the same as to their chemical composition. This great similarity seems also to justify the statement that the carbonization process has been standardized.

In spite of the great avidity of low temperature tar for oxygen no difficulties were met in the analysis by the combustion method. Check results were always obtained proving that the method was reliable.

The tar is the most constant factor of the products of low temperature coking. The coke and gas are the variables and seem to bear a relation to each other. An increase in the carbon of one shows a corresponding decrease in the other. This fact is evidence that low temperature coking does not break down the tar to enrich the gas, but that the coke is used up to increase the gas volume. This is not the case in high temperature coking practice for secondary decomposition of the tar increases the gas yield as well as the carbon yield.

Gas

The data on gas was obtained from Dr. T. E. Layng for the purpose of checking the carbon deposition in the distillation products. For this purpose, the percentages of carbon and hydrogen in coke, tar and gas were reduced to the percent coal basis and a summation made. This summation was then compared to the percent of carbon in the moisture free coal and in most cases fair checks resulted.

No similar check could be used in the case of the hydrogen because the water of decomposition is involved and sufficient data was not at hand.

No interpretation of the data for gas will be attempted.

IV. CONCLUSIONS

1. Ultimate analysis for carbon and hydrogen in coal, coke and tar can be used as a method to check the accuracy of the carbonization process. Variations in the percentage of the carbon in the coal as compared with that of the products were about 1%.

2. The percentages of carbon and hydrogen in any coal may not be used to determine whether a coal will produce a satisfactory coke. If, however, a coal has 5% of hydrogen, the higher percentage of carbon it has, the more nearly will it produce coke of the Pocahontas type.

3. The coke and gas are the variable products from the carbonization process used. A variation in the percentages of carbon and hydrogen in the coke produces a like variation in the gas.

4. The tars produced from the carbonization of any type of coal are of almost constant carbon and hydrogen composition. This indicates that the coals used have been subjected to similar conditions or that the process has been standardized. It is true, however, that since the chemical composition of the products from the different tests on the same type of coal, showed a variance, it is impossible to produce different tests on the same coal, tar, coke or gas of the same composition. The cause is, of course, the complexity of the decomposition reactions involved.

5. Since the carbon and hydrogen percentage in tar produced from any type of coal may be regarded as a constant, we may also regard the volatile products of coking coals to be similar carbon

and hydrogen compounds and to differ only in the quantity of these compounds present in the coal.

Table IX

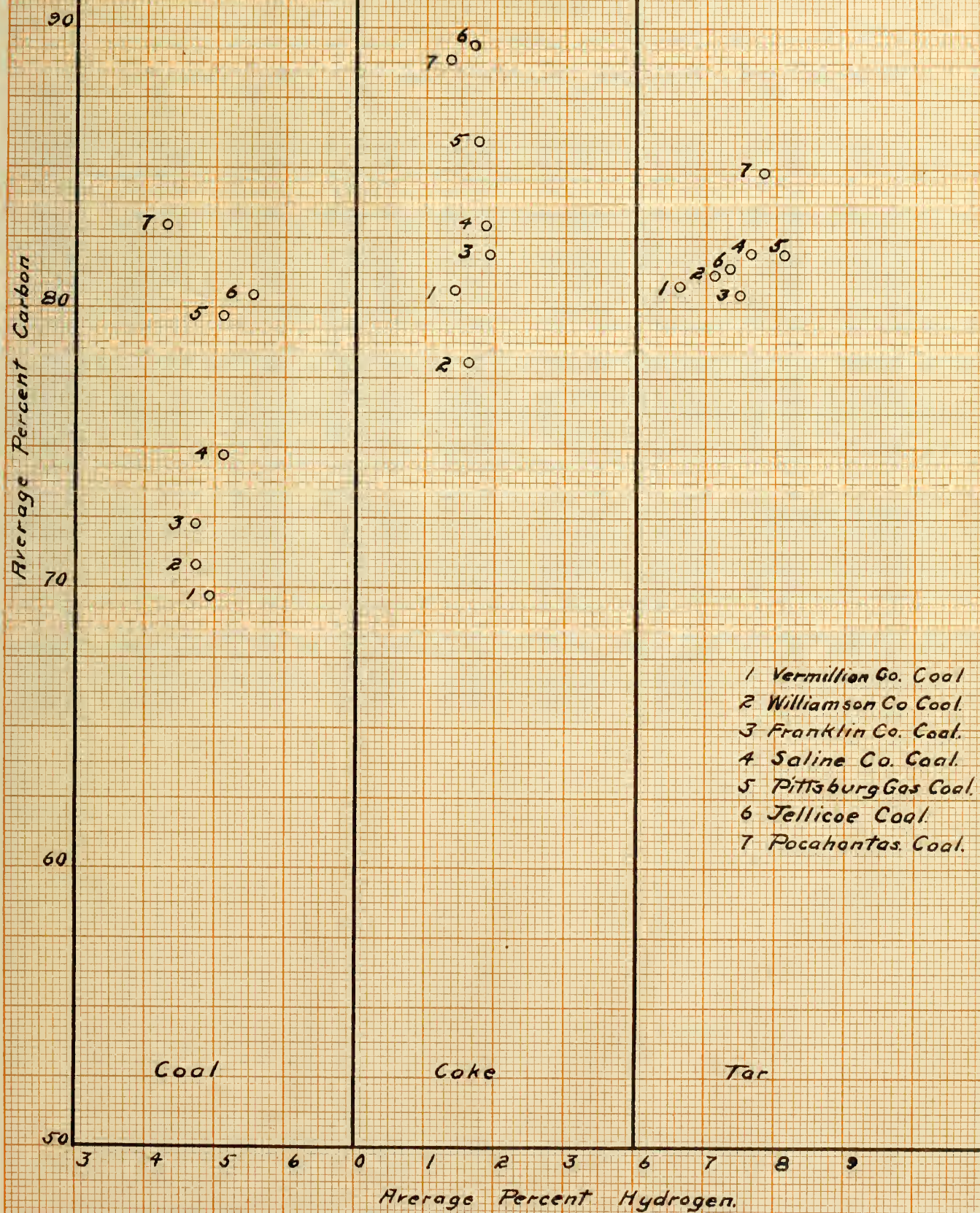


TABLE I
Moisture Free Basis

No.	Coal H ₂ O Free C H	Coke H ₂ O Free C H	Tar H ₂ O Free C H	Gas H ₂ O Free C H
125	73.80 5.05	81.05 1.56	80.60 7.97	6.82 2.78
126	74.50 4.65	80.45 1.81	83.67 6.79	7.10 2.56
128	74.65 5.26	82.75 1.99	80.71 8.00	6.94 2.49
129	74.15 5.31	84.50 1.99	81.42 8.14	6.80 2.30
130	78.50 5.16	85.45 1.73	83.15 8.44	6.69 2.33
131	79.15 4.79	85.00 1.87	84.35 8.22	7.33 2.47
132	80.45 5.05	86.00 1.63	79.59 8.24	7.31 2.08
133	80.25 5.40	87.60 1.72	79.95 8.32	6.55 2.37
134	80.15 5.18	86.75 1.95	82.72 7.43	7.35 2.90
135	83.85 4.18	88.10 1.53	84.34 7.73	4.67 2.29
136	83.35 4.28	88.45 1.42	84.08 6.59	4.24 2.58
137	82.90 4.47	89.60 1.09	88.69 6.08	5.05 2.58
140	70.51 4.93	81.35 1.40	81.14 6.97	5.10 1.79
141	69.40 4.91	79.85 1.47	79.87 6.74	7.27 2.43
142	69.80 5.04	80.65 1.44	81.31 6.28	7.34 2.37
143	80.50 5.58	89.85 1.73	81.77 7.54	9.00 2.88
144	80.40 5.58	89.50 1.64	81.29 7.42	9.42 2.97
145	80.50 5.52	88.65 1.74	81.28 7.12	9.93 3.07
146	75.60 5.25	83.95 1.79	82.05 7.76	7.02 2.42
147	81.50 4.29	88.30 1.46	82.22 6.90	5.31 2.22
148	71.25 5.00	81.00 1.89	79.35 7.67	6.18 1.91
149	73.00 4.42	82.90 1.91	81.00 7.97	5.76 1.97
150	72.40 4.77	81.80 2.04	81.10 6.87	6.33 2.04
151	69.25 4.59	77.00 1.56	82.33 6.81	6.03 2.12
152	69.25 4.59	76.00 1.73	80.65 6.59	6.78 2.21

TABLE II

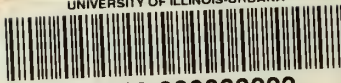
Calculated To Percent Coal Basis

No.	Coal		Coke		Tar		Gas		Sum	Bal.
	C	H	C	H	C	H	C	H		
125	73.80	5.05	58.90	1.13	3.65	.63	7.25	2.93	72.80	1.00
126	74.50	4.65	58.20	1.30	7.72	.63	7.50	3.70	73.60	1.08
128	74.45	5.26	57.40	1.29	8.21	.81	7.29	3.61	72.90	1.55
129	74.15	5.31	57.50	1.35	8.80	.88	7.10	2.40	73.40	.75
130	78.50	5.16	60.85	1.23	9.67	.97	6.91	2.41	77.43	1.07
131	79.15	4.79	61.30	1.35	8.88	.86	7.43	2.50	77.56	1.59
132	80.45	5.05	61.40	1.16	9.48	.98	7.55	2.15	78.43	2.02
133	80.25	5.40	64.80	1.25	9.10	.95	6.75	2.44	80.65	.40
134	80.15	4.18	61.85	1.39	9.52	.85	7.48	2.95	78.85	1.20
135	83.85	4.28	76.00	1.30	2.78	.25	4.75	2.33	83.52	.32
136	83.35	4.47	75.60	1.22	2.73	.21	4.30	2.61	82.62	.73
137	82.90	4.93	75.70	.92	3.04	.21	5.08	2.60	83.82	.88
140	70.51	4.91	58.35	1.00	7.02	.60	6.01	2.11	71.38	.87
141	69.40	4.91	53.30	1.00	6.95	.59	8.43	2.34	68.73	.57
142	69.80	5.04	55.25	.99	6.90	.53	8.68	2.81	70.83	1.03
143	80.50	5.58	60.75	1.17	10.50	.97	9.18	2.93	80.43	.07
144	80.40	5.53	60.20	1.11	9.56	1.05	9.62	3.03	80.00	.40
145	80.50	5.52	60.15	1.18	10.58	.93	10.15	3.14	80.88	.38
146	75.60	5.25	59.10	1.26	8.23	.78	7.52	2.60	74.85	.75
147	81.50	4.29	75.06	1.24	2.39	.21	5.38	2.25	82.76	1.26
148	71.25	5.00	55.85	1.30	7.80	.75	6.65	2.05	70.00	.95
149	73.00	4.42	58.20	1.35	8.01	.79	6.35	2.17	73.16	.16
150	72.40	4.47	56.85	1.42	8.50	.72	6.95	2.24	72.30	.10
151	69.25	4.59	56.35	1.14	7.19	.59	6.55	2.30	70.09	.84
152	69.25	4.59	54.50	1.24	6.97	.57	7.35	2.40	68.82	.43

TABLE III

Name	Numbers
Saline County	126, 128, 129, 146
Pittsburgh Gas Coal	130, 131, 132, 133, 134
Pocahontas	135, 136, 137, 147
Vermillion County	140, 141, 142
Jellico	143, 144, 145
Franklin County	148, 149, 150
Williamson County	125, 150, 151

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